

REPORT DOCUMENTATION PAGE

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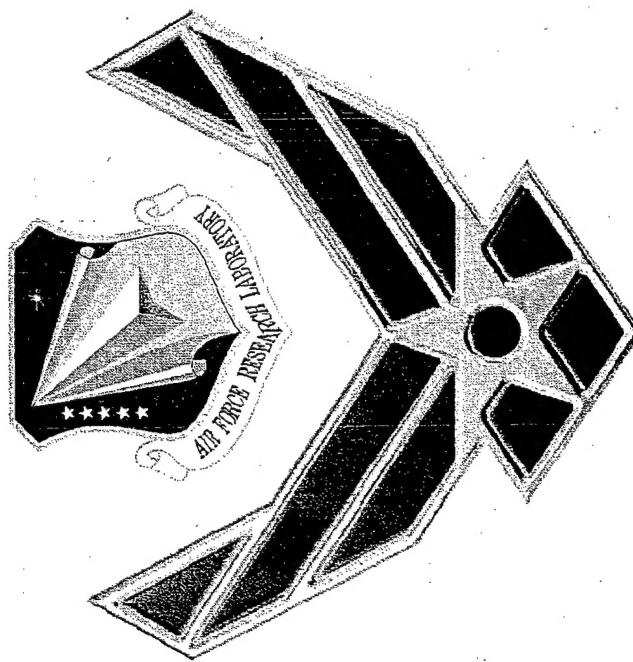
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Computational Studies of Ionic Liquids

AFOSR Ionic Liquids Workshop

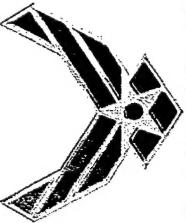
March 7-8, 2004



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Outline



- 1. Introduction**
- 2. Structures and relative energies of
1,5-diamino-1,2,3,4-tetrazolium cation**
- 3. Summary and Conclusions**

Propellants Program

General Approach



Employ a synergic blend of experimental, theoretical, and computational techniques derived from the disciplines of chemistry and physics

Experiments

Develop new synthesis methods

Identify target compounds

Calculate stability and performance

Measure properties & compare with predictions

Attempt synthesis on small scale

Calculate possible synthesis routes

Characterize new materials

Model spectral fingerprints

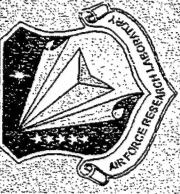
Optimize synthesis, devise test methods

Scale up and test

Transition to Industry

Theory & modeling

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Modeling & Simulation of New Chemical Propellants

Various computational techniques are employed to solve the molecular electronic Schrödinger equation from quantum mechanics:

$$\left[-\frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}} \right] \Psi_{el} = E_{el} \Psi_{el}$$

Is a proposed propellant molecule/material stable?

Structure optimization, verification as local minimum

What is its energy content?

Heats of formation and combustion

How may it be synthesized? How will it react/decompose/combust?

Reaction pathways

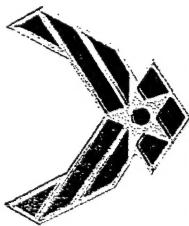
How will we know if we've synthesized it?

Vibrational spectra (IR, Raman, isotopic shifts)

NMR chemical shifts

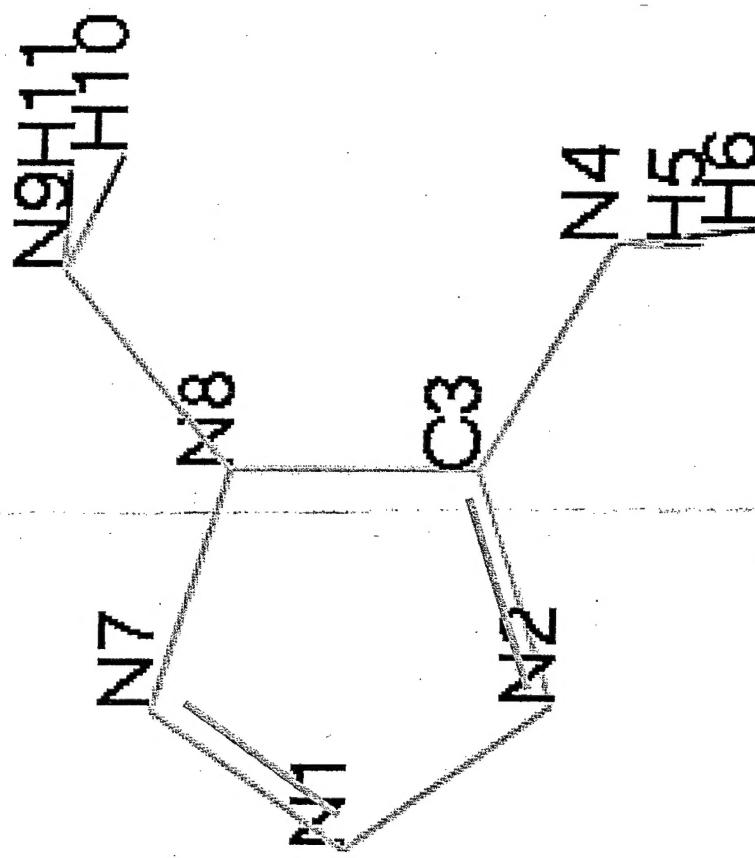
Electronic spectra

1,5-diamino-1,2,3,4-tetrazole

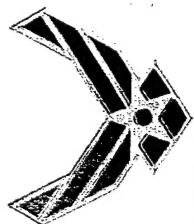


What is the preferred N-protonation site?

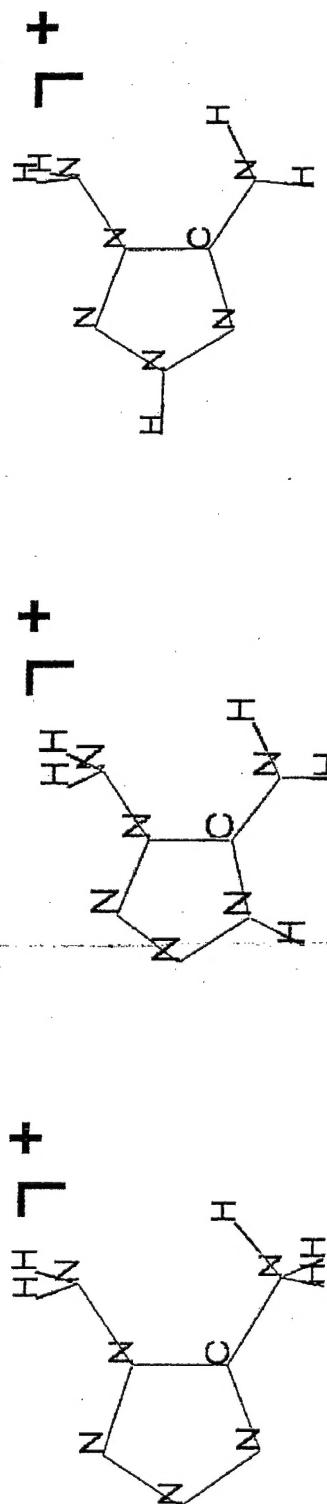
What level of theory is required?



B3LYP(3) Structures and Relative Energies (kcal/mol)

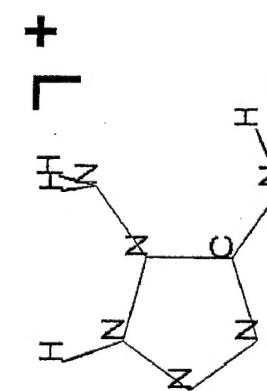


B3LYP(3)/6-311G(d,p) [B3LYP(3)]//aug-cc-pvtz/[B3LYP]



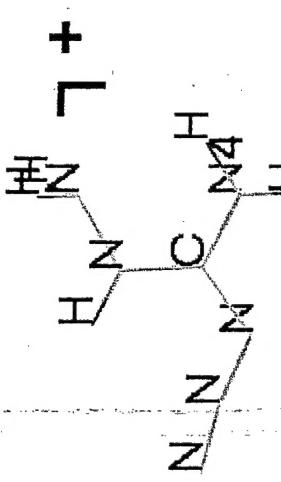
1 (C_s)

35.5 [36.6]



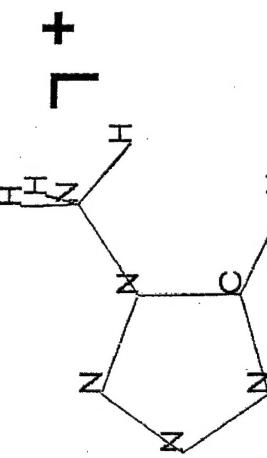
4 (C_s)

18.0 [18.6]



5(C)^s

0.0 [0.0]



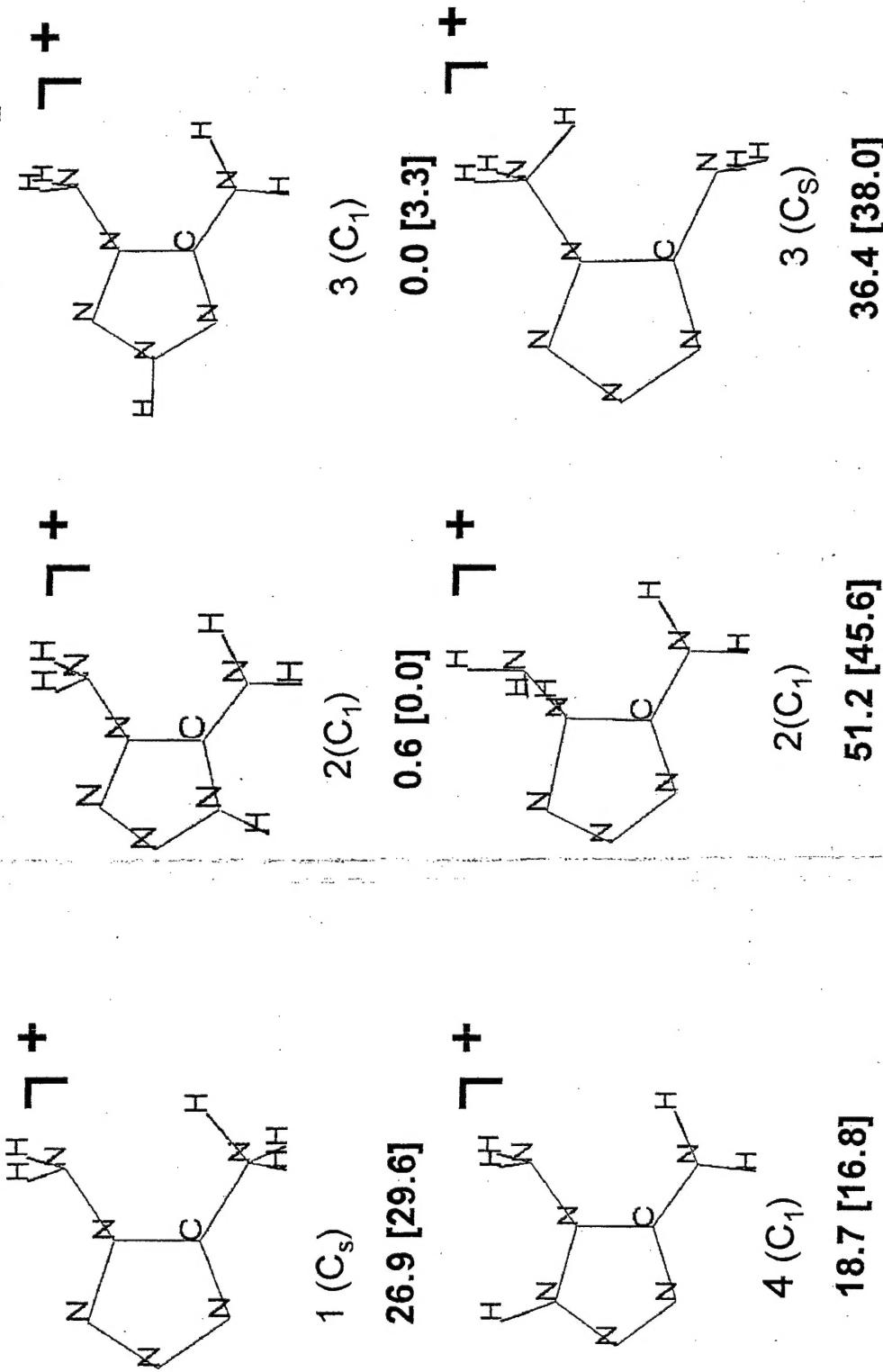
6(c)

42.9 [43.9]



MP2 Structures and Relative Energies (kcal/mol)

MP2/6-311G(d,p) [CCSD(T)/6-311G(2df,p)//MP2]

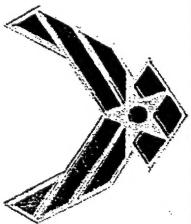


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Summary of Relative Energies (kcal/mol)

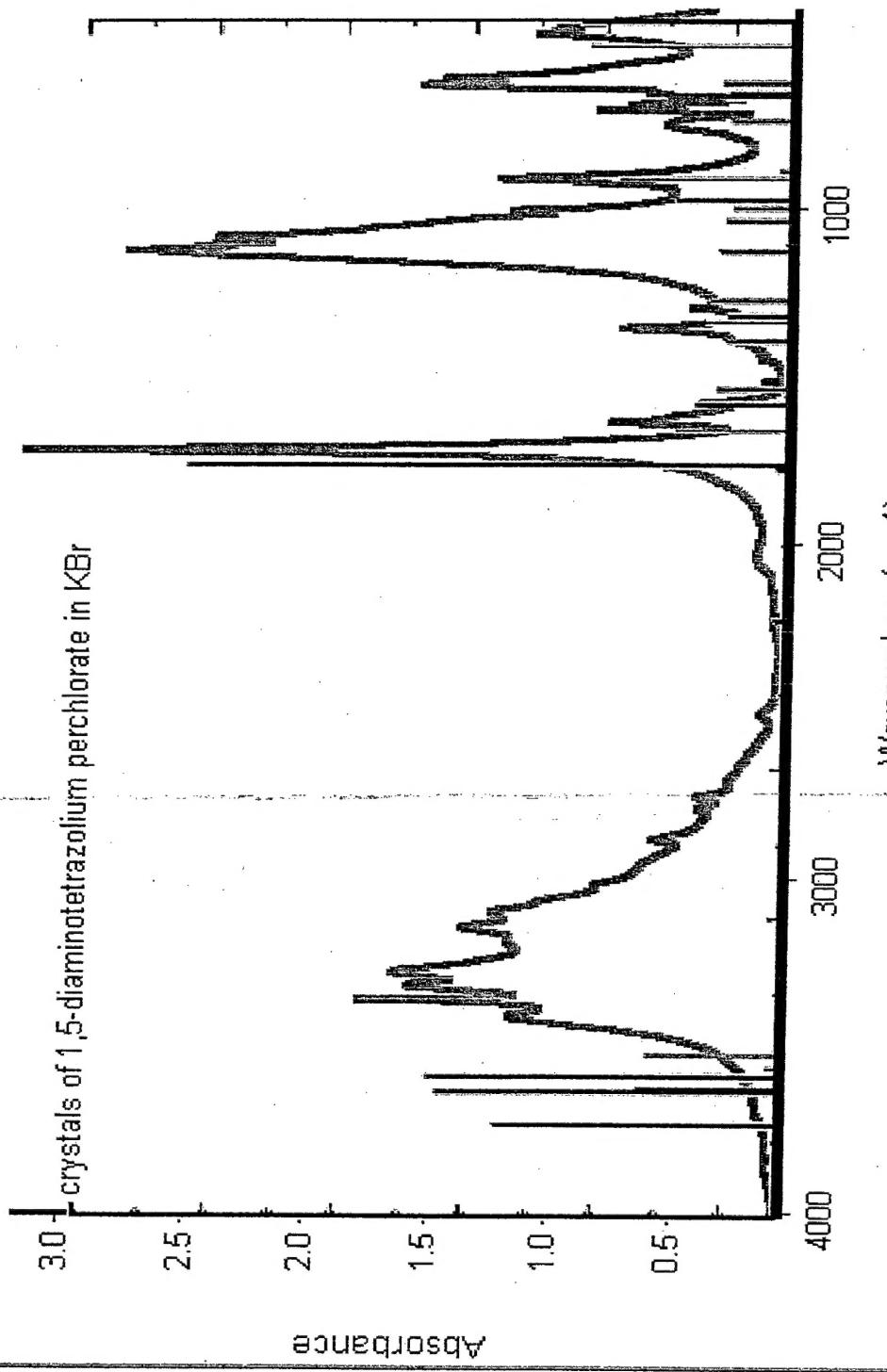
	1	2	3	4	5	6
B3LYP(3)/6-311G(d,p)	35.5	2.1	5.0	18.0	0.0	42.9
B3LYP(3)/6-311G(2df,p)//			TBD			
B3LYP(3)/aug-cc-pvtz//	36.6	3.2	5.6	18.6	0.0	43.9
MP2/6-311G(d,p)	26.9	0.6	0.0	18.7	51.2	36.4
MP2/6-311G(2df,p)//			TBD			
MP2/aug-cc-pvtz//			TBD			
CCSD(T)/6-311G(2df,p)//MP2	29.6	0.0	3.3	16.8	45.6	38.0





Infrared Vibrational Spectra

Comparison of MP2/6-311G(d,p) and experiment



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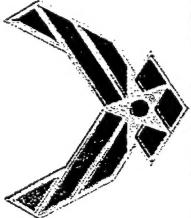
Summary & Conclusions



- The structures and relative energies of the six possible N-protonated structures of the 1,5-diamino-1,2,3,4-tetrazolium cation have been computed at the B3LYP(3)/6-311G(d,p) and MP2/6-311G(d,p) levels of theory. Relative energies have been refined at the B3LYP(3), MP2, and CCSD(T) levels, using the 6-311G(2df,p) and aug-cc-pvtz basis sets.
- Isomers 2 (4H) and 3 (3H) are essentially degenerate at all levels of theory.
- B3LYP predicts isomer 5 (1H) to ring open to form an azide ($\text{NH}_2\text{NHC}(\text{N}_3)=\text{NH}_2$).
- CCSD(T)/6-311G(2df,p)//MP2/6-311G(d,p) calculations predict structure 2 to be the most stable isomer, in agreement with the X-ray crystal structure of the perchlorate salt.



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AFFTC Distributed Center

Army HPC Research Center

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